1. Introduction

In early March 2002, during inspections at the Davis-Besse (D-B) nuclear power station in response to NRC Bulletin 2001-01,[1] boric acid crystal deposits and iron oxide were observed at several openings in the lower service structure support skirt. Follow–up non–destructive examination (NDE) identified axial cracks in five control rod drive mechanism (CRDM) nozzles near the J–groove weld.[2] These cracks had initiated from the inner diameter (ID) of the nozzle and were attributed to primary water stress corrosion cracking (PWSCC). Three of these CRDM nozzles (#1, #2, and #3), located near the center of the reactor pressure vessel (RPV) head, contained through–wall cracks. In addition to the axial cracks CRDM nozzle #2 contained a circumferential crack that had initiated from the outer diameter (OD) of the nozzle.

Repair of these five CRDM nozzles required boring out the lower portion of the CRDM nozzle containing the cracks and the J–groove weld, and re–welding the remaining nozzles back to the RPV head. However, after boring out the lower portion of CRDM nozzle #3, significant degradation of the RPV head base metal was discovered between nozzles #3 and #11. Downhill of nozzle #3, a roughly triangular cavity, ≈127 mm (5 in.) width and 178 mm (7 in.) long and completely through the low-alloy steel RPV head thickness (≈178 mm), had been created.[2,3] A schematic diagram of the D–B RPV head showing the area of RPV head degradation is presented in Fig. 1. A schematic drawing and photograph of the overhead view of the corrosion cavity are shown in Fig. 2. Between 650 and 980 cc (40 and 60 in.^{3}) of metal had corroded and been flushed from the cavity, leaving only a layer of cladding about 7.6 mm (0.3 in.) thick, with an exposed surface area of 130–160 cm^2 (21–25 in.^{2}). Some minor corrosion degradation was also observed in CRDM nozzle #2.[3]

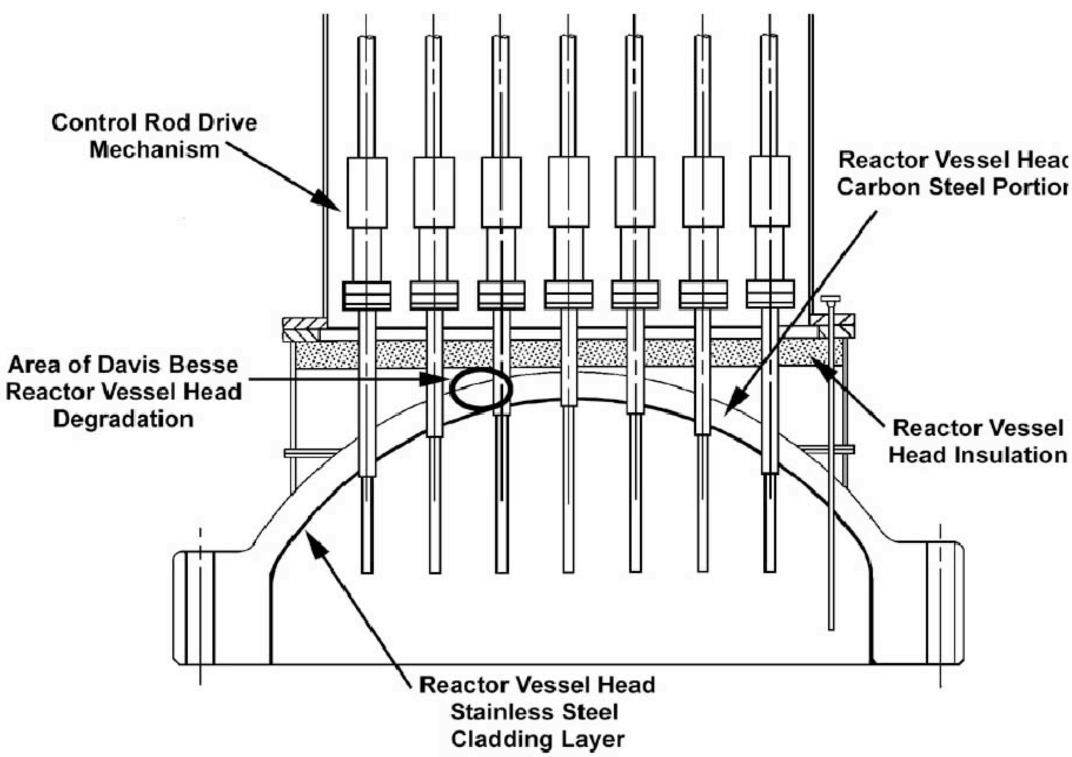

Figure 1. Reactor pressure vessel head at the Davis-Besse nuclear generating station.

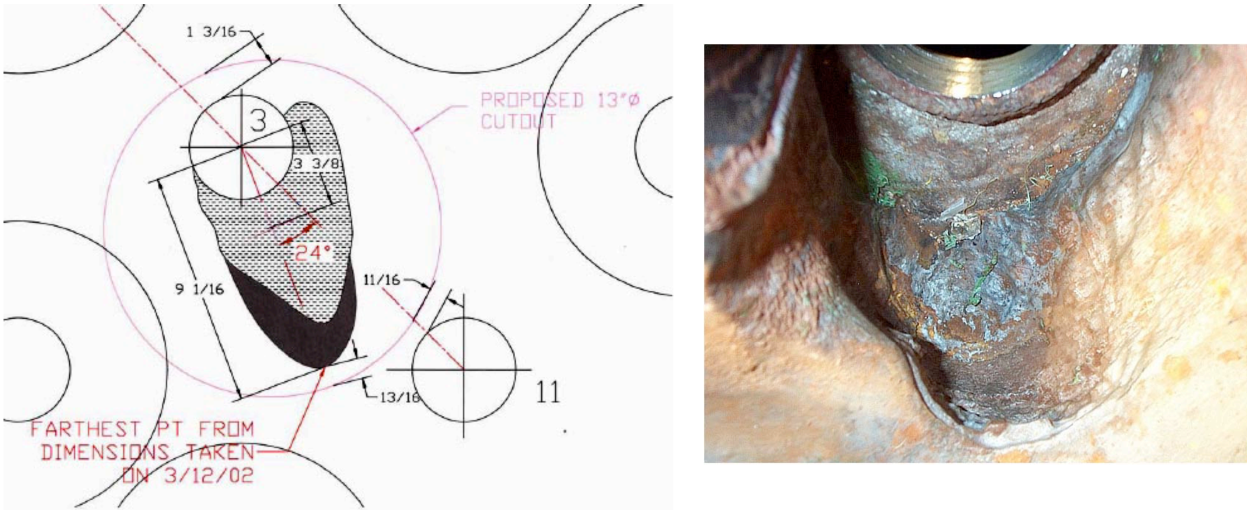

Figure 2. Severe corrosion on the exterior surface of the RPV head between CRDM nozzle #3 and nozzle #11 at the Davis-Besse nuclear power station.

Although PWSCC of Alloy 600 CRDM nozzles is a known degradation mechanism and has been observed at other nuclear power plants,[4] damage of this magnitude to the RPV head had not been anticipated. In the other instances of throughwall cracking of CRDM nozzles, total leakage from the crack into the annulus appears to have been very low and occurred at very low leakage rates. The D-B experience demonstrates that this is not always the case. It is important to understand the conditions that can result in this aggressive attack. The critical issue is why the leaking nozzle #3 at D-B progressed to high leak rates and significant RPV head wastage.

After discovery of the cavity, a root cause report[3] was issued describing the background and events leading up to the discovery, together with a host of "contributing causes" that resulted in the CRDM leaks and the ensuing RPV head corrosion. The root cause report suggests a scenario for the degradation of RPV head base metal:

(a) Crack initiation and growth to throughwall. The report postulates that a crack initiated in nozzle #3 in about 1990 (≈3 years after plant operation began) due to PWSCC. The crack grew to a throughwall crack that penetrated above the J-groove weld in 1994 to 1996. The report hypothesizes that at this stage, the extent of throughwall cracking was very limited and that leakage from the reactor coolant system (RCS) would have been extremely small.

(b) *Minor weepage/latency period.* As the crack grew, RCS leakage would have entered the annular region between the Alloy 600 nozzle and low-alloy steel RPV head. A schematic diagram of the D–B CRDM nozzle is shown in Fig. 3. With addition of moist boric acid from the newly developed crack into the bimetallic annulus, various corrosion and concentration processes (including galvanic attack) would have become possible. The report proposes that these corrosion processes would open the annular gap, although an alternative argument could be made that corrosion products and insoluble precipitation products such as iron metaborate or nickel iron borate could plug the gap and reduce the leakage to very low levels. At this stage, low levels of leakage from the annulus could manifest itself as the classic "popcorn" crust of boric acid deposits. Examples of boric acid deposits from leaking CRDM nozzles are shown in Fig. 4. In contrast to other plants with leaking nozzles, the boric acid deposits on top of the D-B RPV head from leakage from CRDM flange joints could have acted as an "incubator" wherein leaking borated water is retained under the deposits. The identity of the boric acid species within the annular enclave is speculative and could have ranged from aqueous, concentrated solutions of boric acid to molten mixtures of boric acid and boric oxide. The oxygen content of the solution was presumably low, due to the limited access through the annular gap, coupled with the probable egress of superheated steam through the same gap and an uphill pressure gradient.

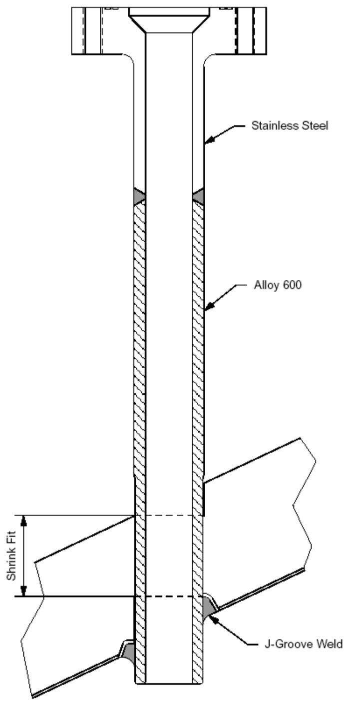

Figure 3.
Schematic of the Davis–Besse CRDM nozzle showing the SS flange, Alloy 600 penetration, and J–groove weld between the RPV head and the penetration.

Figure 4. Deposits of boric acid crystals on reactor pressure vessel head from leaking CRDM nozzles.

(c) *Late latency period.* As the crack continued to grow, the root cause report assumes that the annular gap increased in width and that because the growth in annulus width occurred over a substantial portion of the length around the annulus, the annulus flow area increased faster than the crack flow area. The report ignores any potential plugging of the annulus by corrosion products and insoluble precipitates, thus ensuring that the primary flow resistance would have been due to the dimensions of the crack and not to any restriction offered by the annulus geometry. Under these conditions, oxygen may enter the annulus.

(d) *Deep annulus corrosive attack.* In the scenario envisaged in the root cause report, continued widening of the annular gap would cause the velocity of flow out of the annulus, as well as the differential pressure, to decrease, allowing greater penetration of oxygen and increased corrosion rates. However, calculations of back-diffusion of oxygen against a flow stream presented at the EPRI meeting at Airlie House suggested that even very low flow rates would prevent such diffusion. The root cause report suggests that corrosion was likely to be greater near the crack (D-B nozzle #2) because leakage through the crack would maintain a fresh supply of new reactive oxidizing ions in the boundary layer near the corroding metallic surface.

(e) *Boric acid corrosion.* With high leakage rates, the annulus became filled with an increasing amount of moist steam, partially flashing as it exits. Heat transfer from the surrounding metal is no longer sufficient to immediately vaporize the portion of leakage that does not flash. The metal surface temperature was being suppressed by the cooling effect of the large heat flux required to vaporize the leaking coolant. This effect allowed a greater area to be wetted beneath the accumulations of boric acid. As the crack grew and the leak rate from the crack increased, the corroding annulus began to fill with a saturated boric acid solution. Because the wetted area would be the result of liquid flow, it would be expected to be predominantly downhill from the nozzle. This would result in high corrosion rates and wastage of RPV head material on the downhill side of the nozzle.

The root cause analysis report does not consider the conditions under which the initiation of circumferential cracks from the OD of the CRDM nozzle had occurred. The time line in the report assumes that the crack growth rates (CGRs) in the Alloy 600 are characteristic of those in pressurized water reactor (PWR) primary water. But a PWR primary water environment is not consistent with the observed degradation of the low-alloy steel.

Although it is not possible at present to establish the exact progression of mechanisms that led to the observed RPV head wastage, the degradation modes on the two extremes of the overall progression are known with reasonable confidence. At the extremely low leak rates ($\approx 10^{-6}$ to 10^{-5} gpm) observed in most of the leaking CRDM nozzles, the leaking flow completely vaporizes to steam immediately downstream from the principal flashing location. This results in a dry annulus and no loss of material.

The other extreme is associated with the classic boric acid corrosion mechanism caused by liquid boric acid solution concentrated through boiling and enhanced by oxygen available directly from the ambient atmosphere.[5] The extent of the boiling heat transfer associated with the relatively high leak rate of nozzle #3 was likely sufficient to cool the head enough to allow liquid solution to cover the walls of the cavity. It is clear that relatively high leakage rates from CRDM cracks are necessary for such catastrophic corrosion.

The D-B root cause report provides a scenario that attempts to explain the progression, but the differences between the D-B case and the other CRDM cracking instances are still unclear. The root cause report is incomplete in many regards, partially because much of the data necessary to support the hypotheses simply do not exist. Wastage of low-alloy steel in concentrated boric acid solutions is not well described or quantified in the literature, and especially not under the temperature, flow, and concentration of species that may have existed on the D-B head. The electrochemical potentials (ECPs) of the alloys in the aqueous solutions involved are not known.

This report presents experimental data on ECP and corrosion/wastage rates of the materials found in the RPV head and nozzles of the D–B reactor in boric acid solutions of varying concentrations at temperatures of 95–316°C (203–600°F). Tests were conducted in the following environmental conditions that have been postulated in the CRDM nozzle/head annulus: (i) high–temperature, high–pressure aqueous environment with a range of boric acid solution concentrations; (ii) high-temperature (150–300°C) boric acid powder at atmospheric pressure with and without addition of water; and (iii) low–temperature (≈95°C) saturated boric acid solution both deaerated and aerated. These correspond to the following situations: (a) low leakage through nozzle crack and nozzle/head annulus plugged, (b) low leakage through nozzle crack and nozzle/head annulus open, and (c) significant cooling due to high leakage through nozzle crack and nozzle/head annulus open. The results are compared with the existing corrosion/wastage data in the literature.